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- USSR -

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PROBLEM OF PRODUCING THE DICHLOROANHYDRIDE OF -CHLOROETHYLPHOSPHONIC ACID

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/Following is the translation of an article by Ye. L. Gefter and M. I. Kabachnik in Plasticheskiye massy (Plastics), No 1, Moscow, 1961, pages 63-65./

Dichloroanhydride of β-chloroethylphosphonic acid is a by-product in the manufacture of chloroanhydride and the esters of vinylphosponic acid and also in the reinforcing of phosphorus-containing esters(1).

The following methods are known for producing this compound:

a) the treatment of di-β,β'-chloroethyl ester of β-chloroethylphosphonic acid (DEKhK) by phosphorus pentachloride, or the undistilled product of arbuzovskaya /?/ isomerization of tri-β,β', β"-chloroethylphosphite (technical DEKhK) at 150-160° under pressure(2).

b) the reaction of phosphorus trichloride, dichloroethane, and aluminum chloride with the subsequent hydrolysis of the complex formed(3);

c) the reaction of PCl_3 with ethylene and oxygen(4).

For producing any significant amount of the anhydride of β-chloroethylphosphonic acid the second method is very inconvenient, and the third yields a small amount of the desired product. Thus, the PCl_5 treatment of the product of the isomerization of tri-β,β',β"-chloroethylphosphite is the only practical method of producing the dichloroanhydride of β-chloroethylphosphonic acid. However, the need to use pressure occasions a substantial inconvenience into the process of obtaining the dichloroanhydride in large quantities; carrying out the reaction without pressure, however, diminishes the yield from 70 to 10-13 %, and requires a large excess of PCl_5 (which is extremely unprofitable) -- by 20-22 %.

Considering the foregoing, we studied the possibility of producing the dichloroanhydride of β-chloroethylphosphonic acid with satisfactory yields, without the use of pressure.

We examined two basic approaches:

1. Conversion of DEKhK into β-chloroethylphosphonic acid with subsequent treatment of the acid by various chloroanhydride-forming agents.

2. Conversion of DEKhK into the chloroanhydride, bypassing the formation of β-chloroethylphosphonic acid.

In producing β-chloroethylphosphonic acid it became clear that DEKhK hydrolyzes upon prolonged boiling with concentrated hydrochloric acid (treatment by aqueous and alcoholic solutions of alkali for this purpose is not suitable, as is well known(5)). However, this approach is not helpful since it is subsequently necessary to distill off from the acid obtained a large amount of water and dissolved hydrochloric acid.

A more convenient method is the treatment of DEKhK (pure or technical) by dry hydrogen chloride at 140-160°. Here the ester bonds are easily broken, the dichloroethane formed is distilled off, and there remains in the reaction vessel β-chloroethylphosphonic acid:

$$ClCH_2CH_2PO(OCH_2CH_2Cl)_2 + 2HCl \longrightarrow$$

$$\longrightarrow ClCH_2CH_2PO(OH)_2 + 2ClCH_2CH_2Cl$$

Treatment of the latter with thionyl chloride, phosgene, phosphorus trichloride, and silicon tetrachloride, which have been successful in producing chloroanhydrides of carboxylic acids(6,7), have not shown a positive result. Only the action of $SOCl_2$ in the presence of catalytic quantities of pyridine has resulted in some chloroanhydride. In all the other remaining instances the evolution of HCl has been observed, but the chloroanhydride of β-chloroethylphosphonic acid has not been formed. The conversion of -chloroethylphosphonic acid into its chloroanhydride evidently proceeds through a stage of a polymeric anhydride: $ClCH_2CH_2PO(OH)_2 \longrightarrow (ClCH_2CH_2PO_2)_n \longrightarrow ClCH_2CH_2POCl_2$, and the above-mentioned relatively weak agents in practice form only the first stage of this process.

Treatment by phosphorus pentachloride, and also simultaneous reaction of phosphorus trichloride and chlorine smoothly converts β-chloroethylphosphonic acid into its chloroanhydride with yields of up to 80 % of the theoretical:

$$ClCH_2CH_2PO(OH)_2 + 2PCl_5 \longrightarrow (2PCl_3 + 2Cl_2)$$

$$\longrightarrow ClCH_2CH_2POCl_2 + 2POCl_3 + 2HCl$$

Also studied has been the possibility of a direct conversion of DEKhK into the chloroanhydride of β-chloroethylphosphonic acid.

The action of $SiCl_4$, $COCl_2$, PCl_3, and $SOCl_2$ on DEKhK at various temperatures has not led to the desired result.

The action of phosphorus pentachloride on DEKhK at 140-150°, especially in the presence of several catalysts, has brought about a sharp increase in the yields of chloroanhydride of β-chloroethylphosphonic acid from 10-13 % to 80 %. The action of these catalysts on the carbon chain is well-known(8), and recently these have been patented for the production of the chloroanhydride of vinylphosphonic acid(9).

Of considerable important is the order of steps in carrying out this reaction. Heating the mixture of DEKhK and PCl_5, and also the addition of DEKhK to PCl_5 at different temperatures results in such a serious insufficiency that the evaporating dichloroethane -- to the extent of its formation -- and the evaporating phosphorus oxychloride carry off with them a considerable amount of phosphorus pentachloride, which leaves the reaction zone.

Upon the gradual introduction of PCl_5 into the heated DEKhK with a small addition of iron chloride, copper chloride, aluminum chloride, and others, together with an energetic stirring of the mixture, all of the PCl_5 which enters into the reaction zone interacts with DEKhK, breaking both ester bonds. From the dichloroethane, phosphorus oxychloride, and chloroanhydride of β-chloroethylphosphonic acid that are formed, the first two components are mainly distilled off in the course of the reaction, and the residue and the desired product are separated by vacuum distillation. The yield: 80 %. Instead of pure DEKhK the dry product of the isomerization of tri-β, β', β"-ethylphosphite may be used in the reaction. Here the yield stands at 65-70 %.

The attempt to use in place of phosphorus pentachloride, phosphorus trichloride and chlorine, is not successful: under the reaction conditions a significant amount of the PCl_3 introduced decomposes with the evolution of yellow phosphorus.

Experimental Part /See Note/

/Note: L. S. Ludentsov participated in the experimental work./

All operations in the production and isolation of the chloroanhydride of β-chloroethylphosphonic acid must be protected from moisture in the air.

The constants of the chloroanhydride obtained and the data of its analysis are cited only once in order to avoid repetitions.

Technical β-chloroethylphosphonic acid

An excess of dry hydrogen chloride was passed through 540 g of technical DEKhK. The process was carried out at 150-160° with strong agitation of the reaction mixture for a period of ten hours. 372 g of dichloroethane was collected (theoretical amount: 396 g). In the flask 305 g of dry β-chloroethylphosphonic acid (according to theory -- 289 g) was left behind -- a dark viscous liquid with an acid number 751 (calculated acid number is 776).

Chloroanhydride of β-chloroethylphosphonic acid from β-chloroethylphosphonic acid and PCl_5

a) To 72 g of technical β-chloroethylphosphonic acid 209 g of PCl_5 was gradually added; the addition was accompanied by heating up to 50-60° and a profuse evolution of hydrogen chooride. The reaction was heated to 80°, at which time the phosphorus oxychloride was distilled off, and the residue was then vacuum-distilled. The fraction with the boiling-point range of 60-100° (1.5-2 mm) was distilled once more and 64 g (70 % of the theoretical) of the dichloroanhydride of β-chloroethylphosphonic acid was obtained with a b. p. = 78-80° at 4 mm; n_D^{20} = 1.4992; d_4^{20} = 1.5440. The literature values(2): b. p. = 68° at 2 mm; n_D^{16} = 1.4977; and d_4^{16} = 1.5430. The amount of hydrolyzable chlorine found was 39.04 %. $C_2H_4OPCl_3$. The calculated amount of hydrolyzable chlorine was 39.1 %.

b) Hydrogen chloride is passed for six hours through 135 g of pure DEKhK at 150-160°. The yellow liquid obtained, with an acid number of 766 is treated with 209 g of PCl_5, as in the preceding experiment. 75 g (82 % of the theoretical) of the dichloroanhydride of β-chloroethylphosphonic acid was obtained.

Chloroanhydride of β-chloroethylphosphonic acid from β-chloroethylphosphonic acid, PCl_3, and chlorine

To a mixture of 72 g of technical β-chloroethylphosphonic acid and 69 g of phosphorus trichloride a stream of dry chlorine was passed along with stirring and external cooling, maintaining the temperature of the reaction mixture at 45-55°. The excess of chlorine was displaced by carbon dioxide and the reaction mixture was distilled as described above. 61 g (67 % of the theoretical) of the chloroanhydride of β-chloroethylphosphonic acid was produced.

Chloroanhydride of β-chloroethylphosphonic acid from β-chloroethylphosphonic acid and thionyl chloride

To a mixture of 55 g of technical β-chloroethylphosphonic acid and 1 g of pyridine there was gradually added with vigorous agitation 100 g of thionyl chloride; the reaction mixture temperature was kept at 40-45°; to complete the reaction the mixture was heated at 70-75° for one hour, and then the volatile fraction was distilled and the residue was then vacuum-distilled. 21 g (30.5 % of the theoretical) of the chloroanhydride of β-chloroethylphosphonic acid was obtained. There remained in the distillation flask a large amount of resinous residue, which decomposes upon further heating.

Chloroanhydride of -chloroethylphosphonic acid from DEKhK and PCl_5

To a mixture heated to 140-150° containing 68 g of pure DEKhK and 0.9 g of water-free iron chloride there was gradually added, with vigorous stirring, 110 g of PCl_5. Thereupon, the dichloroethane and phosphorus oxychloride formed were distilled off. Then the reaction product was vacuum-distilled.

The fraction with a boiling-point range of 50-95° (2 mm) was distilled once again and yielded 36.4 g (80 % of the theoretical) of chloroanhydride of β-chloroethylphosphonic acid, boiling at 80-82° (4 mm). When technical DEKhK (under the same conditions) was used, 65 % of the chloroanhydride was produced.

When copper chloride was used as the catalyst (with technical DEKhK) the yield of the product desired stood at

50-55 %, and when the reaction was carried out without a catalyst the yield was 25-30 % of the theoretical.

Conclusions

A preparative method has been developed for obtaining the chloroanhydride of β-chloroethylphosphonic acid without the use of pressure and with yields of approximately 65-70 % of the theoretical when the technical grade of the di-β,β'-chloroethyl ester of β-chloroethylphosphonic acid was used, and with yields of approximately 80 % when the pure grade was employed.

LITERATURE

1. Ye. L. Gefter, Plast. massy, No 5, 47 (1960).
2. M. I. Kabachnik and P. A. Rossiyskaya, Izv. AN SSSR /Izvestiya Akademii nauk SSSR -- Bulletin of the Academy of Sciences USSR/, OKhN /Otdeleniye khimicheskikh nauk -- Division of Chemical Sciences/, 515 (1946).
3. A. M. Kinnear and E. A. Perren, J. Chem. Soc., 3437 (1952).
4. L. Z. Soborovskiy, Yu. M. Zinov'yev, and M. A. Englin, DAN SSSR /Doklady Akademii nauk SSSR -- Reports of the Academy of Sciences USSR/, 67, 293 (1949).
5. M. I. Kabachnik and P. A. Rossiyskaya, Izv. AN SSSR, OKhN, 403 (1946).
6. I. Guben, Methods of Organic Chemistry, No 2, ONTI, /Ob"yedinyunnyy nauchno-tekhnicheskiy institut -- Joint Scientific-Technical Institute/, 1935, p 478.
7. K. D. Petrov, P. A. Moshkin, and I. P. Losev, Khim. prom. /Khimicheskaya promyshlennost' -- Chemical Industry/, No 6, 22 (1945).
8. Kyrides, J. Am. Chem. Soc., 55, 1209 (1933); L. M. Smorgonskiy, ZhOKh /Zhurnal organicheskoy khimii -- Journal of Organic Chemistry/, 17, 416 (1947), etc.
9. K. Schimmelschmidt and W. Denk, patent -- German Federal Republic 1023034; RZhkhim /Referativnyy zhurnal khimii -- Abstract Journal for Chemistry/, 1960, abstract 39631.

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